Energy Crops

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Contributor: Mariana Abreu , Luís Silva , Belina Ribeiro , Alice Ferreira , Luís Alves , Susana M. Paixão , Luísa Gouveia , Patrícia Moura , Florbela Carvalheiro , Luís C. Duarte , Ana Luisa Fernando , Alberto Reis , Francisco Gírio

Energy crops are dedicated cultures directed for biofuels, electricity, and heat production. Due to their tolerance to contaminated lands, they can alleviate and remediate land pollution by the disposal of toxic elements and polymetallic agents. Moreover, these crops are suitable to be exploited in marginal soils (e.g., saline), and, therefore, the risk of land-use conflicts due to competition for food, feed, and fuel is reduced, contributing positively to economic growth, and bringing additional revenue to landowners.

herbaceous species | forest crops | microalgae culture | marginal soils | degraded soils | contaminated soils | chemical process | biochemical technologies | thermochemical process | energy potential

1. Introduction

Dedicated energy biomass production, the so-called energy crops, has experienced a rapid expansion in some countries, mostly related to the use of agricultural crops (mainly annual crops), for liquid biofuels production. Energy crops are species that can be produced to generate energy as electricity/heat or biofuels, helping to reduce the generation of greenhouse gases (GHG) mainly by the energy and transport sector [1], due to their inherent photosynthetic capabilities and renewable characteristics. Moreover, their exploitation can help countries achieve energy security and contribute to local and regional development and growth [2], by serving as a source of income for many agricultural producers [3]. In addition, these species should not be considered for food and feed like tubers, grains, and maize, among others [4], to avoid competition for food, feed, and fuel. Moreover, energy crops represent alternative biomass for supply to biorefineries. Moreover, lignocellulosic species for second-generation fuel production [5] and non-food species, represent an important feedstock for many industrial uses.

The advantages of energy crops are also applicable to lignocellulosic residues (part of the species not suitable for harvesting), such as straw, bark, leaves, and bagasse from herbaceous species and long fiber and hardwood from forest species. The reuse of any type of biomass waste material such as forest waste (e.g., wood waste from the wood industries and manufacture of pulp and paper), secondary waste (e.g., animal waste, organic material from food companies, solid waste) and agricultural residues (e.g., short-rotation species, cereals, among others) [6] allow reducing both the fuel load deposited in landfills and the still latent dependence on fossil-based feedstocks [7], creating several environmental, social, and economic opportunities. To comply with sustainability criteria, energy crops value chains must present a reduction of GHG emissions when compared to those released by fossil-based value-chains; the biomass production must not affect or alter negatively the quality of groundwater, soil, or air, and for this reason, it is necessary to limit or to avoid the use of chemical products such as fertilizers and pesticides, the biodiversity of the area where the species are planted must be protected to avoid negative effects directly or indirectly, and, finally, at the local level, the crops must not compete with the food sector and, in parallel, should encourage the economic and social growth of the region [6][8][9].

Herbaceous crops, like the giant reed, switchgrass, reed canary grass (*Phalaris arundinacea*), miscanthus, and perennial ryegrass (*Lolium perenne*) are crop species that can be cut annually after planting and the rhizomes must be left in the ground to ensure continued growth, a procedure that can be maintained for 15 years or longer, therefore, they are also classified as perennial crops. The perennial energy crops (or multi-annual plantations) do not need the incorporation of considerable quantities of pesticides and fertilizers, they help to avoid soil erosion, present low soil fertility requirements [10], and help in the recycling of organic components in the soil [11]. The short cycle coppice like poplar (*Populus* spp.), eucalyptus (*Eucalyptus* spp.), paulownia [*Paulownia tomentosa* (Thunberg) Steudel], and willow (*Salix* spp.) are woody species characterized to be fast-growing and can be cut and regenerated every 3 to 5 years over a 25-year period, with the purpose of obtaining in a short time high yields for energy generation [5]. Microalgae also present high potential as an energy crop because they can accumulate sugars and oils for later direct conversion to biofuels (e.g., bioethanol).

These types of crops when grown in soils with low Indirect Land Use Change (ILUC) risks, namely, soils considered as Marginal/Degraded/Contaminated (MDC), release environmentally clean emissions, and, as compared with fossil fuels, they once represented a negative impact on the atmosphere concerning the quantity of produced carbon dioxide (CO_2) [10]. Yet, these species cannot be cultivated on agricultural terrain with a high carbon (C) soil quantity [5], rather appropriate agricultural and forestry models of these plantation crops should be created [4], and when liquid, solid, and gaseous biofuels are produced (in some cases), the organic by-products can be used as animal feed and fertilizers [10], as a way of continuing the raw material cycle.

2. Conversion of Low ILUC Risk Energy Crops to Biofuels

2.1. Herbaceous and Other Crops

Herbaceous crops were chosen because they are species that present several environmental benefits such as high nutrient and water use efficiencies, erosion control, soil stabilization, and carbon storage, they contribute to the landscape and biological diversity and have a low need for inputs, namely fertilizers and pesticides [10][12][13][14][15][16], and help in the recycling of organic components in the soil [11]. For example, miscanthus presents an extensive and deep rooting system, a lengthy permanence in soil, and the translocation of nutrients from aerial biomass to the rhizomes at the end of the vegetative cycle, which reduces the need for high application of fertilizers to ensure growth [17]. Jerusalem artichoke is a low-energy intensive crop with several advantages over traditional agricultural crops (grain crops) including rapid growth, elevated biomass generation, and low external production costs (e.g., it needs a low amount of fertilizer, pesticides, or water [18]). All these species are also more widely known from an agronomic point of view and from a commercial point of view they are already on the market, some more present than others.

Virginia fanpetals [*Sida hermaphrodita* (L.) Rusby] is a crop that has aroused great interest by many researchers, mainly in Northern Europe, because it is a species that easily adapts to the climatic conditions of these regions and acts as a phytoremediator [19] in contaminated soils with HMs [20], soil poor in organic matter, and in rocky and sandy soils, and it stores carbon in its roots (hence underground) allowing GHG mitigation [21]. *Sida hermaphrodita* has high potential as an energy crop in solid fuel production such as pellets [22] being burned in combustion processes and for biogas (or biomethane) production [19][20][21][23], and it is also suitable for the formation of by-products such as fiber, forage, and in pharmaceutical applications [19]. Based on these characteristics, it can be said that Virginia fanpetals is a potential competitor for the herbaceous energy crops that are included in this work. Currently, it is not cultivated in the territory of Portugal, so it can be risky to implement it in the country, however, there is no doubt that for future work, it would be very interesting to develop a study on the viability of this species in Portugal, to investigate its possibilities and increase list of new cultures with potential in the territory as an ILUC crop.

Another advantage of herbaceous crops is that they can be implemented in Wastewater Treatment Plants (WWTP), e.g., *Cynara cardunculus*, giant reed, hemp, linseed, and sorghum. Moreover, some crops can have multi-products, e.g., paper pulp production (giant reed, hemp, miscanthus, sorghum, and switchgrass species), which can help to alleviate the excessive exploitation of eucalyptus. These crops, e.g., sorghum, present also the ability to capture big quantities of CO_2 from the atmosphere, converting it into sugars [24], thus helping to mitigate climate change.

Herbaceous species also present some constraints. For example, crops that have biomass characteristics that are not favorable for energy use, e.g., cardoon due to the amount of N. Giant reed is considered invasive, which can legally prevent its implementation as an energy crop, and for this reason, it is necessary first to use what already exists and then to implement it in a controlled manner. Some crops also present limited yields with low rainfall, and this can compromise production in Mediterranean countries. Even for the production of those crops in soils with low ILUC risk, there are still some barriers to their promotion for energy purposes: e.g., hemp presents legal impediments to its production in many countries, and in other countries, there is a significant market competition in seed use for food purposes, and the suitability of the stalk to several applications with significant commercial value should also be noted. Linseed oil can also be used in the production of vegetable oils for the food sector, a factor that may limit its great expansion as an energy crop, however, when the plantation is applied in soils not suitable for agriculture, its final destiny will be always to produce biofuels or by-products.

The chemical composition of the different herbaceous and oilseed crops is presented in **Table 1**, for easier comparison between them.

Table 1. Chemical composition of herbaceous and other crops.

Energy Crops	Cellulose (% w w^{-1})	Hemicellulose (% w w^{-1})	Lignin (% w w^{-1})	Ash (% w w^{-1})	Extractives (% w w^{-1})	Other Components (% w w^{-1})
Cynara cardunculus (stalks) [7][25]	34	18.5	(14–23)	(5–11)	(13–21)	-
Cynara cardunculus (seeds) [26]	-	-	-	-	-	Fat content (17–24), protein (26–30), and fiber (20–28)
Arundo donax [6][27][28]	(21–45)	(7–36)	(6.7–34)	(2.3–8)	(12–22)	-
Cannabis sativa [7][29]	(33–74)	(7.6–16.6)	(2.2–29)	(2.6–7.6)	(3.7–20)	(0.3–23.1)
Helianthus tuberosus (tubers) [6][30][31][32]	(28.5–49.4)	(10.2–16.8)	(14.5–22.2)	4.7	12.1	N (1.45–1.55)
Linum usitatissimum [33]	-	-	-	-	-	Fatty acids [stearic (2–4), palmitic (4–7), linoleic (35–40), oleic (25–40), and α-linolenic (25–60)]
Miscanthus × giganteus [6][28]	(43–58)	(16–34)	(5.8–11)	2	(9–17)	-
Sorghum bicolor [7][24][34]	(23.7–44.6)	(20–27)	(4.4–24.7)	0.4	-	-
Panicum virgatum [7][34][35][36]	(31.8–45)	(20.3–36) [xylan (25–27)]	(7.4–31.2)	(3.2–5.7)	-	-

As can be seen in **Table 1**, species such as cardoon and linseed have the potential for biodiesel production since oil can be obtained from the seeds. Another species that also has this characteristic, despite not being specified in the table, is hemp, as oil can also be obtained from the seed. Due to the amount of cellulose and hemicellulose (polysaccharides) present in each species, all herbaceous species have the potential for second generation bioethanol production.

For biodiesel production, the species that have potential as raw materials are cardoon, hemp, Jerusalem artichoke, linseed, and sorghum. Comparing the different crops, hemp is the one that presents a higher yield in oil. [37][38].

Species such as cardoon, hemp, Jerusalem artichoke, giant reed, miscanthus, sorghum, and switchgrass can be applied in biochemical technologies (anaerobic digestion (AD) and alcoholic fermentation) and thermochemical processes (combustion and pyrolysis). Based on studies and related data, some crops, such as sorghum from ensiled sorghum forage [39][40] and giant reed [41], show promising potential for AD technology. In the case of bioethanol, some crops, such as hemp [42] and JA species [43] have also shown promising potential. Biohydrogen production is another promising option, for example, through the exploitation of cardoon and sorghum bark [44].

Herbaceous crops also show promising results with thermochemical processes, such as pyrolysis of miscanthus [45]. Regarding the hydrothermal processes, crops like miscanthus and sorghum have shown potential. Through hydrothermal liquefaction (HTL), it is possible to obtain biochar and bio-oils, with good yields, for example, when sorghum is the feedstock [40][46].

2.1.1. Cardoon (*Cynara cardunculus* L.)

Cynara cardunculus is a herbaceous perennial crop [47], belonging to the family Asteraceae, order Asterales, and class Magnoliopsida [48]. The seed productivity can attain 1.3 t ha^{-1} [49].

Traditional use, knowledge, and application of *Cynara cardunculus* are not recent. In the Mediterranean regions, aqueous extracts of cardoon flowers are utilized for human consumption, as coagulants in the traditional fabrication of sheep's milk cheeses, giving them unique characteristics of excellence in texture and taste [50]. The cardoon residues can be utilized for the food sector in the generation of natural preservatives and in the case of oil extracted from the cardoon seed, the surplus material that represents a considerable amount, namely, 81 g 100 g^{-1} of seeds, can be applied as animal feed or as biofertilizer [51]. On the other hand, cardoon leaf infusions are known in folk medicine for regulation of the hepatobiliary system [52], as an anti-inflammatory, antiviral, antimicrobial, antioxidant, antihyperglycemic, antidiabetic, antiproliferative, antibacterial, and anti-HCV, among others [51]. The cardoon stalks are utilized in the paper factories due to the fiber content (cellulose) that can be found in this material [53]. Other applications are the use of cardoon to obtain phytochemical compounds for the pharmaceutical sector (polyphenol-rich sheets that have also been applied in the cosmetic industry [54]), in the fresh green forage production for animal feed, and as reinforcement in structural composites, among other wide variety of uses [50]. It is also possible to obtain a great diversity of bioproducts from *Cynara cardunculus*, such as biolubricants, bioplastics, fragrances, personal hygiene materials, and household items, among others [55]. New uses have been given to various substances that make up the different constituent parts of cardoon, such as obtaining dietary fibers, including inositol, hemicellulose, inulin (fructose polysaccharide extracted from the roots [54]) and cellulose pectin, minerals, and sesquiterpenes lactones such as cynaropicrin, among others [51].

The cardoon is considered a species with high biomass yield with a huge potential for bioenergy production, namely, biodiesel (as cardoon is one of the species with the highest generation of fatty acids) [56], biomethane [57], and bioethanol [47], as well as other processes such as thermochemical [47] like combustion, gasification, and pyrolysis [50], biohydrogen [58], and solid biofuel [50][59] production. Another application is the biokerosene generation from cardoon biomass pyrolysis in which it is possible to achieve a 34.72% yield [60].

Biodiesel production from yeast using the cardoon stalks as raw material within a biorefinery model was studied by Barbanera et al., 2021 being also made a Life Cycle Assessment (LCA) study from the cradle-to-gate for assessing the environmental factors. It was concluded that this type of biodiesel has great environmental advantages, as the emissions of GHG are −1.5 g CO_{2eq} MJ^{-1}, being negative because of the positive credits that the by-products provide [61]. In another study, the obtainment of biodiesel and biolubricants was studied, also in a biorefinery model from cardoon oil, being applied to the transesterification process with methanol and other more complex alcohols (e.g., 2-ethyl-1-hexanol and 2.2-dimethyl-1,3-propanediol). The biolubricants were obtained from fatty acid methyl esters (FAMEs) from cardoon oil with the most complex alcohols. However, to ensure that this type of oil is promising on a large scale (biorefinery), it is required to increase the oxidative capacity of biodiesel (1.35 h). In relation to other materials, the biolubricant yields that are admissible and higher than 92% are also obtained for products with high commercial value such as glycerol and in the case of methanol, this can be reused [62].

Biomethane production through the anaerobic digestion (AD) process was evaluated using cardoon as raw material, using two cultivated species and one wild type. The cultivated species were allowed to obtain higher amounts of both biomass and biomethane, producing 19.1 and 16.8 t DM (dry matter) ha^{-1} $year^{-1}$ and a biomethane volume of 4074 and 4162 Nm^3 when compared to 11.8 t DM ha^{-1} $year^{-1}$ and 2867 Nm^3 of biomethane obtained with wild cardoon. Therefore, *Cynara cardunculus* is considered to be an energy crop with great potential for implementation in biomethane production [63].

The high potential of *Cynara cardunculus* biomass to produce bioethanol [64] has been well studied. Ethanol-water (EW) pre-treatment was implemented for the fragmentation of lignocellulosic biomass present in the cardoon to improve the glucose yield after enzymatic saccharification. A high yield of glucose was obtained (around 72%) after 60 min, at 190 °C, with a liquid/solid ratio of 20 L kg^{-1} and ethanol concentration of 25%, with possible retention of glucans greater than 97%, as well as the removal of xylans greater than 68% and lignin greater than 58% [65]. The thermochemical pre-treatment of cardoon biomass using sodium hydroxide (NaOH) is a very efficient hydrolysis method to obtain a maximum value of methane yield between 0.5 up to 0.6 L methane g^{-1} VS [66]. The alkaline extraction after Cardoon Steam Explosion Pre-treatment (CSEOH) allows for obtaining an ethanol concentration of 18.7 g L^{-1}, with 66.6% of fermentation efficiency and a yield of 26.6 g ethanol 100 g^{-1} CSEOH or 10.1 g ethanol 100 g^{-1} of untreated material (cardoon) [67]. In another study, two processes were studied separately after Steam Explosion (SE) pre-treatment, namely, Semi-Simultaneous Saccharification and Fermentation (SSSF) and Separate Hydrolysis and Fermentation (SHF). SSSF allowed obtaining a yield of ethanol of 13.64 g of ethanol 100 g^{-1} of cardoon, a value slightly higher than that of SHF (13.17 g of ethanol 100 g^{-1} of cardoon) as well as a shorter processing time of 24 h for SSSF, when compared to the SHF [68].

Currently, the application of cardoon to Wastewater Treatment Plants (WWTP) has been of great importance. The behavior of the *Cynara cardunculus* when wastewater (WW) and digested sewage sludge were applied in a Spanish plantation, specifically, in Alcázar de San Juan, was evaluated, aiming at the implementation of this technology for thermal energy production. Five parcels of 100 $m^{2\ w}$ were evaluated, each one with different irrigation, namely, drinking water taken as the control, treated WW, 1 t ha^{-1} of air-dried sewage sludge, 2 t ha^{-1} of air-dried sewage sludge, and 0.7 t ha^{-1} of commercial inorganic fertilizer. The moisture and heating value (High and Low) of cardoon in each parcel were determined. The moisture was in the range [2.08–3.63%] and the Lower Heating Value (LHV) and Higher Heating Value (HHV), were in the following ranges [3.68–3.84) kcal kg^{-1} DM (HHV) and [3.41–3.56] kcal kg^{-1} DM (LHV), respectively. As the difference was not significant, they concluded that it is possible to obtain a similar quantity of energy when the cardoon is irrigated with WW and sewage sludge or commercial fertilizer. The unique problem that can be found in the sewage sludge is the high salinity, thus, it is important to make a continuous characterization of this material [69].

In Portugal, cardoon was proposed for guaranteeing high productivity in the territory, namely, an area of 72,313 ha (0.81% of the total area in Portugal's mainland which corresponded only to degraded and marginal lands), with low requirements concerning the soil and water type, and included energy production in several biochemical and thermochemical technologies [70].

2.1.2. Giant Reed (*Arundo donax* L.)

Arundo donax L., also known as giant reed (family Poaceae, order Cyperales, and class Liliopsida), is an erect, reed-like grass, herbaceous, perennial cane, aggressive and invasive species with the capacity to reproduce quickly, either by seed propagation or by vegetative propagation, being a primary threat to native riparian habitats worldwide and out-competing native plant species in the access to soil-water.

Giant reed is a poly-annual culture that presents average yields of 15 to 40 t DM ha^{-1} $year^{-1}$ [6][27][28]. This species can be applied for energy generation [71], paper pulp, and fiber production (e.g., cellulose for rayon fabrication), and is widely used as an ornamental material for basket-work manufacture, barriers to gardens (trellises and garden fences), crude shelters, construction and roofing materials, livestock fodder, fishing rods, and arrows. Medicinally, the rhizomes and roots have been used for many uses, and culinary uses of the young shoots and leaves, and the rhizome have been proposed [71][72]. It has been also planted along ditches and drainage canals for erosion control or as a bank stabilization agent. Although well known as an aggressive invasive species, the wide commercial applications of *Arundo donax* wide will contribute to further development and adoption of this crop, bearing in mind that the exploitation of this species and its invasive character requires careful reflection [73][74]. With the constant search for biofuels that is expected to increase over time, it is anticipated that the latent interest in this giant reed, considering the high yields it presents, will increase.

Data collected by Corno et al., 2014 show that the giant reed presents major biomass productivity in comparison with other energy crops, allowing a higher generation of biofuel and energy per unit area. Therefore, it can substitute other energy crops, with a diminution in the cost of biomass production. However, there is very little data about the utilization of *Arundo donax* for energy and biofuels generation, therefore, so much remains to be explored [75].

The conversion of *A. donax* into bioenergy has been carried out either by biochemical pathways or thermochemical conversion routes. The biomass of *A. donax* can be used for three types of bioenergy: solid biofuels (in briquettes and pellets including direct biomass combustion [76]), biogas, and biomethane production has been proposed by [77][78][79], and bioethanol [80][81][82][83].

The giant reed represents an adequate species for the biorefineries when its wide utilities are considered. A dedicated *A. donax* crop was subjected to hydrothermal pre-treatment by Di Girolamo, Grigatti, Barbanti, and Angelidaki, 2013 to analyze its potential for biogas generation. Three different situations were applied: without catalyst, during a time (24 h) of substrate impregnation, utilizing 2% w w^{-1} sulfuric acid (H_2SO_4), and instant incorporation of 2% w w^{-1} H_2SO_4 previous steam cooking for pre-treatment parameters; temperature between 150 °C up to 180 °C and time from 10 to 20 min. The results of batch digestion tests, made with 4 g VS L^{-1} on thermophilic conditions, namely 53 °C, during 39 days, presented a methane yield of 273 mL g^{-1} VS incorporated for unprocessed biomass. The no catalytic reactions of biomass reached a yield of 23% for a temperature of 180 °C and a duration of 10 min. The reactors that treated catalyzed biomass were experiencing methanogenic inhibition. This type of inhibition can be caused by the competition with the sulfate-reducing bacteria (SRB) [41]. For Mediterranean conditions, *A. donax* could be an interesting choice as feedstock for biogas facilities [83], concerning profitability, a plant size of 300 kW was referred to as the most beneficial for bioenergy production from *Arundo donax*.

According to Maucieri et al., 2019, the highest biomass, ethanol (3.5 t ha^{-1}), and methane yields (8227 m^3 ha^{-1}) in a four-year study were obtained with *Arundo donax* among thirteen pluri-annual herbaceous cultures previously chosen for their potential biomethane and bioethanol production. This highlighted *A. donax* as one of the most interesting species for biofuel production [6].

The pre-treatment of *Arundo donax* biomass is required for bioethanol production but as this step has been considered the most energy demanding, this should be accounted for in any life-cycle energy balance [83]. Muthuvelu et al., 2019 evaluated giant reed as a novel source of sustainable lignocellulosic residues for bioethanol generation utilizing ultrasound-assisted alkaline pre-treatment. *Arundo donax* presented 214 ± 3 mg g^{-1} maximum reducing sugar release, yielding a fermentation efficiency of 83 ± 7% [84].

A microwave–alkali-assisted pre-treatment in one stage has been proposed for *A. donax* pre-treatment with some added benefits, such as less energy consumption, fast heating, and less toxic compound production. The utilization of 5% NaOH solution yielded the highest sugar monomer yield (6.8 g per 100 g of biomass) [85].

Ba, Liu, Wang, and Yang, 2020 carried out pyrolysis studies of *Arundo donax* as feedstock and well as a final potential study of giant reed for alternative sources of materials, energy, and chemicals calculated according to average biomass productivity and marginal soils area in China. An industrial scale (2000 t day^{-1}) would yield 28 MW power, 51.36 t day^{-1} bio-oil, 555.04 t day^{-1} vinegar, and 511.36 t day^{-1} biochar from 9 million t of feedstock obtained in 0.3 million ha of marginal soils at a predicted 30 t ha^{-1} year^{-1} [86]. Moreover, soil remediation and sewage decontamination near aquatic bodies would also occur as *A. donax* was an excellent species to advance the quality of water-polluted bodies and contaminated lands [87], which is of particular significance for the further development of dedicated biorefineries [86]. Finally, Fernando, Barbosa, Costa, and Papazoglou, 2016 concluded that *A. donax* had the big production levels among nine studied species, comparatively an energy balance positive together with the lowest GHG emissions, low nutrient requirements, and the lowest cost per ton of dry biomass or per unit of energy for Mediterranean conditions [87].

The economics of energy crops have been neglected or, to some extent, limited in the literature. The economic aspects of *A. donax* were analyzed from a systematic survey of publications by Jámbor and Török, 2019. Giant reed was proven to have a high potential for a cost-effective biomass generation either in marginal or disadvantageous small areas due to favorable yields and energy balance, high Capital Expenditure (CAPEX) but low Operational Expenditure (OPEX), making its production attractive and potentially economically sustainable (biomass supply and generated revenue) [83].

According to the same publication, giant reed presented the second-highest energy production cost (2.34 € GJ^{-1}), but the highest nutrient-use yield for phosphorus (P) and nitrogen (N) among several studied energy crops. This suggests that *A. donax* is a clear option to utilize further to convert WW (as a source of N and P) into biofuels in the frame of the circular bioeconomy.

2.2. Forest Crops

Forests crops like the short cycle coppice such ss poplar (*Populus* spp.), paulownia [*Paulownia tomentosa* (Thunberg) Steudel], and willow (*Salix* spp.) are woody species characterized to be fast-growing, can be cut and regenerated every 3 to 5 years in a 25-year period, with the purpose of obtaining in a short time high yields for energy generation [5]. This species also serves as protection for many more sensitive areas and in a wide diversity of soils, avoiding in some cases an increase in erosion. They are highly viable for converting into bioenergy and can be used to produce a variety of by-products (information that is confirmed and described in the main text of each culture) which brings numerous advantages for their implementation as feedstock for biorefineries. Based on their characteristics, namely, low S, N, and Cl amounts, the use of ligneous biomass for energy purposes has environmental benefits compared to herbaceous biomass, in particular regarding NO_2 emissions. Another advantage is related to a lower risk of corrosion phenomena in combustion boilers [88].

The advantage of forest crops is that the species like acacia that are invasive crops could be used for biofuel production because they reduce the occupied area, control the reproduction of this species [89], minimize the cost of the removal of this species, and reduce the fuel load that can generate fires in sensitive areas [90]. Acacia dealbata allows a wide variety of products to be obtained, such as the production of paper pulp, like the paulownia and willow species. Other advantages of forest crops are that they can reduce erosion in the areas where they are planted, as seen with the poplar, and their extracts show less inhibitory effects on the fermentative processes of bioethanol production, with higher efficiency for conversion into biofuels compared to other species such as pine (softwood) [91]. Moreover, trees like poplar also present a low ash content and a high amount of cellulose (greater than corn straw and switchgrass [92]). These trees can also retain leachate from landfills and be applied in WW treatment [93], as in studies with poplar and willow. *Populus nigra* has a high value from a bioeconomic perspective, being widely used in the creation of new hybrids in Europe such as *Populus* × *Euramericana* (*Populus deltoites* × *Populus nigra*), and they are fast-growing energy crops with greater advantages [94]. An advantage of the willow is that it is an excellent phytoremediator because it removes between 40% and 80% of nitrate-nitrogen compounds present in groundwater, being a species that serves as a regulator of the chemical composition of the water and the functioning of the soil [95].

Forest species also present some constraints such as acacia which presents an invasive character, an aspect that causes a loss of biodiversity by changing ecosystems and creating competition between species [96]. Additionally, acacia requires well-drained soils [97]. *Pinus pinaster* presents a high concentration of N and S, these elements could generate atmospheric pollutants in combustion systems [98]. Moreover, the main species causing fires in Portugal are *Acacia dealbata* and *Pinus pinaster* [99]. There are food applications that use food-grade grown willow, however, willow produced from marginal lands and, especially contaminated soils, may prevent the usage of its biomass for food and feed purposes.

The chemical composition of the different forest crops is presented in **Table 2**, for easier comparison between them.

Table 2. Chemical composition of forest crops.

Energy Crops	Cellulose (% w w^{-1})	Hemicellulose (% w w^{-1})	Lignin (% w w^{-1})	Ash (% w w^{-1})	Extractives (% w w^{-1})	Other Components (% w w^{-1})
Acacia dealbata (wood) [100][101]	(42.4–50.9)	(17–29) [xylan (16.4–19.3)]	(19.3–20.1)	(0.5–1.1)	(3.1–5.85)	-
Acacia dealbata (bark) [100][101]	19	21.6	18.6	3.3	37.5	-
Acacia dealbata (leaves and flowers) [100][101]	43.1	(21.6–22.2) [xylan: 18.7]	25.9	(0.5–1.1)	8.3	-
Pinus pinaster [102][103]	[40–50]	[15–24]	[25–33]	0.16	2.9	-
Paulownia tomentosa [104][105][106][107][108]	(39.2–49)	(17.98–28.1)	(17.8–37.6)	(0.5–4.6)	(5.6–8.8)	Holocellulose (39.2–61.5)
Populus [92][109]	(42–49)	(16–23)	(21–29)	1.8	-	-
Salix viminalis [110][111][112][113][114][115][116]	(37–56)	(13–26.7)	(12–37.4)	(0.6–2)	(6.3–7.75)	Holocellulose (63.7–64.5)

As can be seen in **Table 2**, all the forest species studied [acacia (wood), maritime pine, paulownia, poplar, and willow] present a high cellulose and hemicellulose (polysaccharides) content, and therefore they all have the potential for second generation bioethanol production. All these species also present a high potential for combustion systems because they present a low ash content facilitating the conditions applied inside the boiler, without the need for continuous cleaning of the ash.

In biochemical technologies such as AD and alcoholic fermentation, maritime pine, poplar, and willow have shown potential. However, acacia and paulownia are also considered suitable raw materials for bioethanol production [108]. Some forest species have also been tested for biohydrogen production, with promising results, e.g., paulownia stalks [117].

These forest species described in this entry have also the potential for energy production (electrical, thermal, or both), e.g., in combustion processes as solid fuels (woodchips, pellets, and briquettes), for example, the ones produced from maritime pine [118]. Additionally, they can be used to produce bio-oil through pyrolysis, e.g., with acacia [119] and paulownia [120].

In relation to other thermochemical systems like gasification, species such as maritime pine [121], poplar [122], and willow can serve as a raw material in this process. Or in hydrothermal process, e.g., with willow.

2.2.1. Acacia (*Acacia dealbata* L.)

Acacia-mimosa (family Fabaceae/Leguminosae, order Fabales, and class Magnoliopsida) with the scientific name *Acacia dealbata* Link is an allochthonous or introduced woody tree with a large shrub and erect stem [97].

Acacia-mimosa plays an important commercial role since its wood can be used for the paper production through the kraft process by the amount of cellulose present in the material [101], allowing the elaboration of several products like cardboard, the paper for writing and printing, which gives it a special shine, considered of high quality, and more advantageous than eucalyptus due to the low amount of alkali it presents [97], and finally, acacia wood is also used for the production of construction materials and furniture, compounds of interest to the medicinal sector [123][124], xylooligosaccharides [125], syringaldehyde, vanillin [126], and solutions rich in glucose [127][128]. The bark is used for the production of tannins (substances of plant origin) due to the high amount present in the species (greater than 74%) [129] and other compounds such as absorbents [130], those with an antimicrobial and antioxidant capacity [100][131] and the anti-quorum sensing [132]. In the perfume industry, flowers are processed to produce fragrances, as well as perfume fixatives [97], in the production of compounds with anti-inflammatory properties [133][134] as well as other types of products such as bioherbicides [135]. In the ecosystem, the pollen in the flowers presents a relevant function for the continuity of sleep [97]. The extracts from the leaves of *Acacia dealbata* are excellent as a raw material in natural products beneficial to health due to their antioxidant activity [100][136], and the antimicrobials present in the extract [136] are also used for herbicides production [135]. Concerning the timber sector, acacia is considered of high quality for the manufacture of furniture and poles and is also used as fuel for heat generation. Two liquid biofuels that can be produced from *Acacia dealbata* [97] are bioethanol [137][138] and bio-oil. Some studies researched the implementation of acacia for bioproducts and biofuels production in a biorefinery-type system, either from the residual material of the species [139] or from all constituent parts of the species [140].

Muñoz et al., 2007 studied the pre-treatment with two fungi (*Ceriporiopsis subvermispora* and *Ganoderma australe*) maintained at a temperature of 27 °C, moisture of 55% for 30 days, and the organosolv delignification was performed at 200 °C, with 60% of ethanol for 1 h. In this first phase, the pulp yield in the case of acacia was between 31% and 51% and obtained 93% of glucan and 2% of lignin. With the objective of producing bioethanol, it was applied to the pulp material with two process types SSF or SHF being utilized for the *Saccharomyces cerevisiae*. For the SHF and SSF processes, the best conversion to bioethanol was obtained for acacia in the first process from 40% to 48%, and in the second process, it was 44% to 65%. These results concluded that each stage must be improved to obtain a higher conversion of this species into bioethanol, namely, in the pre-treatment through a decrease in the incubation time and in the stage of saccharification/fermentation to utilize a material with a higher pulp consistency [141].

Another study that evaluated the possibility of producing bioethanol with *Acacia dealbata* through a diluted acid pre-treatment, with this phase the most important because it is where the transformation of the lignocellulosic material in sugars for bioethanol production occurs. It was evaluated for two different systems: SHF and SSF, which included a wash with residual Water Insoluble Fraction (WIF). The *Acacia dealbata* presented a high potential to produce bioethanol with 10.31 g ethanol L^{-1} obtained during 24 h with the SHF process and with the other process, SSF, it obtained 7.53 g ethanol L^{-1} over 48 h, so, under these conditions, SHF obtained the best results. However, it is possible to obtain 12.18 g ethanol L^{-1} when the fermentation is made over the soluble fraction of undiluted water in parallel with the SHF process [142].

To evaluate the potential of *Acacia dealbata* in a biorefinery, this species was submitted to an ionic liquid 1-ethyl-3-methylimidazolium acetate pre-treatment for 30 min at a temperature of 150 °C, with 66% of the xylan (20 times higher when compared to untreated raw material) recovered and 88% of cellulose (13 times higher than untreated material). The remaining solid part (substrate) was processed in an enzymatic hydrolysis system (cellulose conversion) for 48 h, which allowed obtaining high yields of fermentable glucose (carbon source) suitable for the biofuels generation like bioethanol and other bioproducts [128], therefore, the application of acacia in an industrial scale system such as a biorefinery is guaranteed.

In Spain, a study was carried out in which several *Acacia dealbata* plantations were evaluated (by the high invasive degree of this species in the south of Galiza and north of Portugal) to characterize the species in relation to the moisture content, volatile percentage, HHV and LHV to determine its energy potential, in several constituent parts of the species such as the trunk and the thin leaves and branches. According to the values obtained, the average moisture content (35.29% for the trunk and 35.22% for the leaves and branches); volatiles (83.58% for trunks and 77.28% for leaves and branches); ashes (0.80% for the trunk and 2.32% for the leaves and branches) and HHV when the material is free of water (without moisture) is 4797.93 kcal kg^{-1} for the trunk and 5181.10 kcal kg^{-1} for the leaves and branches. In turn, the LHV is 4478.65 kcal kg^{-1} for the trunk and 4865 kcal kg^{-1} for the leaves and branches. With these results, the viability of acacia-mimosa as fuel in combustion systems for heat production or in cogeneration systems, due to the values obtained of the calorific power [143] is guaranteed.

In Portugal, the main species for producing wood pellets for burn-in boilers is the *Pinus pinaster* and for this cause, it is important to compare this type of material with other species like acacia-mimosa for the quantity of material that can be found in the territory [96]. It can serve as a carbon reservoir because it is a fast-growing species, it also rapidly removes the carbon present in the atmosphere through CO_2, mitigating climate change, thus confirming its potential for the production of material with high carbon content [144] such as biochar that can be obtained through the pyrolysis process at 450 °C for 8 h [145].

An acacia plantation with 2 ha can yield 140 t of biomass for wood pellets production that has a similar quality to those produced with *Pinus Pinaster* Aiton and *Eucalyptus globulus* L., with the only exception being the amount of Cl which was slightly higher [89]. In another study, on the contrary, it was found that the chemical composition (ash content, N and Cl) of *Acacia dealbata* and *Eucalyptus globulus* are the main factors that hinder their use for producing certified pellets. The use of the waste material of these species serves as a solution for the collection and reuse of the material, and it should be used in processes where certified products are not required [146], creating a system that complies with the criteria governed by the circular economy. In a fluidized bed reactor with a turbulent regime, two different types of pellets were burned: one produced with maritime pine and the other with acacia-mimosa, and the contaminants [CO_2, CO, and nitrogen oxides (NO_x)] formed in each case were verified and compared. The pellets produced by both species presented a lower emission of contaminants and a better combustion behavior due to the type of reactor used (fluidized bed) [147].

Vicente et al., 2019 analyzed the emissions of pellets produced from Acacia seen as an invasive species in Portugal, specifically located in the coastal areas, to be utilized like fuel at a residential level. Among the properties evaluated were the particulate matter PM_{10} (anhydrosugars like levoglucosan 284 µg g^{-1} PM_{10} and polyaromatic hydrocarbons 8.77 µg g^{-1} PM_{10}), CO (2468 ± 485 mg MJ^{-1}), sulfur dioxide (SO_2) (222 ± 115 mg MJ^{-1}), and NO_x (118 ± 14 mg MJ^{-1}). All these values were considered elevated because the acacias trees were grown in zones with high salt concentrations. For this reason, to obtain a solid fuel from acacia with minor production of emissions, the pre-treatment of the material before the pelleting including the drying step must be optimized, mixing the acacia with other materials to obtain a biofuel with other properties, to incorporate additives that allow major compaction of the particles and to control the air supply during the combustion [148].

In another study, Amutio et al., 2013 evaluated several types of wastes from *Cytisus multiflorus* (50%) and *Spartium junceum* (50%) both identified as Bio1, *Acacia dealbata* identified as Bio2, and, lastly, *Pterospartum tridentatum* identified as Bio3 in the pyrolysis technology. The process occurred in a Conical Spouted Bed Reactor (CSBR), with a temperature of 500 °C, continuous biomass input in the system, and continuous removal of the char. In the liquid phase, the bio-oil (main product) was constituted of water, phenols, ketones, acids, furans, and a lesser quantity of saccharides, aldehydes, and alcohols. The results showed that the yield of bio-oil was 79.5% (Bio1), 72.1% (Bio2), and 75.1% (Bio3) being higher for the Bio1 due to the higher quantity of hemicellulose and cellulose in this species, that favors the bio-oil production. The char yield was 16.6% for Bio1, 23% (Bio2), and about 20% for Bio3. In the relation to the gas phase, the quantity produced was between 4% and 5% for the three species. These results showed the high benefits of these species for the bio-oil generation in a CSBR reactor, being possible to maximize the yield of the liquid phase with high heat and mass transfer rates, a low residence time of the volatile elements, and continuous removal of char, conditions that were maintained in this process [119].

2.2.2. Maritime Pine (*Pinus pinaster* Aiton)

Pinus pinaster Aiton is a woody fast-growing species [149] belonging to the family Pinaceae, order Pinales, and class Pinopsida, which requires a lot of insolation and is able to resist shade only in the first months after germination [150].

This species presents a fundamental function in the economics and rural development in the commercialization of wood, namely for carpentry in exterior and interior areas (floors and parquet), as well as in the real estate sector for the high quality of the material, wood treated for the production of poles, scaffolding shipyards, packaging and pallets for the storage and transport of goods, bodyworks [149], fiber and particle agglomerates in the phosphorus industry, in the manufacture of fence fencing, toys, blinds [151], in the pulp production through the amount of cellulose present in the trunk, of resin for the generation of a great range of chemical products by the presence of terpenic oils of good quality [152] and firewood, in their simple form for the production of heat at the domestic level. Other uses applied to this species are in the manufacture of poles, furniture, and building materials like particle boards [153] and they serve as shading for recreation and picnic areas. The resin is utilized to make rosin and turpentine, the main components in the production of soaps, glues, oils, waxes, medicines, and varnishes. The bark is used to produce tar [154], polyphenols, tannin, antioxidants, adhesives, bio-oil, and particle boards (from the bark partially liquefied) [155].

Maritime pine can be used for several biofuels production using the biochemical process like biogas and bioethanol and in thermochemical conversion [156] through solid fuels production of pellets [157][158] and briquettes in heating, gasification, and pyrolysis systems. *Pinus pinaster* is the principal material in the pellets production in Portugal as it is made of soft wood, an aspect that facilitates grinding, due to its low ash content and greater amount of extractives when compared to other species such as Eucalyptus [157], and because of the availability of the species in the territory.

Pinus pinaster wood was studied for its viability for biofuel production in a biorefinery. The pre-treatment for the material was carried out for aqueous fractionation to obtain the hemicellulose saccharides solution (liquid) and another phase, the solid-state composed of cellulose and lignin. The liquid solution (constituted for polymeric or oligomeric hemicellulose saccharides) was treated with H_2SO_4 (up to 4 wt%) and heated (up to 130 °C) to transform substrates into sugars. The saccharification was achieved almost totally under certain conditions for possible fermentation. After the solid phase (conversion of cellulose) is mixed in the acid medium under microwave irradiation, levulinic acid is obtained to produce valeric biofuels and formic acid for further use in the fuel cell. In the case of the lignin, it was recovered like solid residue using a method with acid [159].

The main species causing fires in Portugal are *Genista tridentata*, *Cistus ladanifer*, *Cytisus* spp., and *Acacia dealbata* (species that make up the first mixture), coming from marginal lands, and *Pinus pinaster* and *Eucalyptus globulus* (constituting the second mixture) integrated into the forest system, therefore, it was proposed to study the fractionation of each mixture as feedstock in a biorefinery for a year, to assess their potential to produce biofuels and other bioproducts. Each mixture was subjected to an autohydrolysis between 190 °C and 240 °C (non-isothermal conditions) to compare the two: the effects of fractionation of each mixture (solubilization of hemicellulose in oligosaccharides and the achieved recovery of lignin and cellulose), the heating values obtained to evaluate their potential as biofuel, and the behavior of enzymatic cellulose hydrolysis for the glucose formation. Excellent results were obtained for both mixtures, such as high oligosaccharide recovery, HHV (the solid part can be used as fuel), and improved glucose obtention (from 45% to 90%) [99]. This type of mixture represents a suitable material for biofuel production (including bioethanol) and products of high commercial value in a biorefinery-type installation, being seen as an alternative to reduce the material load causing fires.

A study about the heating values from different species, allowed researchers to know what species are most significant to solids biofuel production, namely, wood pellets. It was evaluated that several species like *Castanea sativa*, *Eucalyptus* *globulus*, *Quercus robur*, *Salix babylonica*, *Populus* × *canadensis*, *Pseudotsuga menziesii*, maritime pine, among other types, were classified as softwoods and hardwoods. The results show that hardwoods had an HHV between 17,631.66 and 20,809.47 kJ kg^{-1} and the softwoods had values ranging from 19,660.02 to 20,360.45 kJ kg^{-1} (the value for the maritime pine is 20,237.89 kJ kg^{-1} i.e., below the species with the highest HHV). In relation to the LHV, the hardwoods had a value between 14,411.54 and 17,907.85 kJ kg^{-1} and the softwood values were between 15,629.71 and 16,935.72 kJ kg^{-1}, with the last value corresponding to the maritime pine, namely, the highest LHV. The study considers the *Pinus pinaster* to be one of several species having the best conditions for application in the thermochemical processes, mainly, combustion [160].

In the District of Bragança in Portugal, a study was conducted on the energy generation (electricity and heat) from the maritime pine because it is a forest species most common in this region. The destination of the energy produced includes several sectors (residential, service, and industrial). The total forest area in Bragança of the *Pinus pinaster* is 89,024 ha with an energy content of 4170.5 TJ. However, consider the data of a power factory, 22% of efficiency, a heating value of 18 GJ t^{-1}, and an operation time of 7200 h $year^{-1}$ which can obtain electricity power of 254.9 GWh. Consider the annual yield of this species, and it can be concluded that it is possible to supply the Bragança District with almost 49% of energy and 60% of its electricity demands for each sector, and 84% of the total energy demands of the several sectors mentioned before [161].

In Spain, the study by Álvarez-Álvarez et al., 2018 was made with the purpose of investigating the potential of different species including maritime pine. the maritime pine obtained the values as follows: the highest HHV of 19,366.277 kJ kg^{-1} (mean); the lowest value of ash of 0.602%, and in the ultimate analysis; the percent of C, sulfur (S), and N were 47.775% C, 0.650% S, and 0.494% N. Once again, it can be concluded the importance of *Pinus pinaster* in the energy production for the HHV and ash values, although the high concentration of N and S are elements that generate atmospheric pollutants [98].

Viana, Rodrigues, Godina, Matias, and Nunes, 2018 performed the analysis and evaluation of several characteristics such as density, moisture, proximate and ultimate analysis, HHV, energy density (E_d), Fuelwood Value Index (FVI), and a dimensional value, among others. The most important results obtained for the different parts analyzed of the maritime pine (wood stem, pine needles, and top of the specie) were: 0.22% to 1.92% of ashes, 19.57 to 21.61 MJ kg^{-1} of HHV, 2.06 to 8.9 GJ m^{-3} of E_d, and the values of the FVI were superior in the case of the wood stem (4658) and top of the species (2861.8). Based on these results, it is guaranteed that the maritime pine represents a biomass with a very high potential to create energy in the form of woodchips, briquettes, and pellets [118].

Following the previous study, one of the co-authors, Leonel Nunes, published another work where the woodchips produced from maritime pine were analyzed but it also incorporated the bark. It is important to highlight that in almost all species, the bark contains a very high amount of inorganic material that contributes to the superior values of the ashes. Later on, some problems can arise in the industrial boilers and during the combustion as the bark can cause, the incrustation of the scobs in the bottom of the equipment, a factor that increases the number of times that it is necessary to undertake maintenance requiring the boiler to stop [162].

Several types of materials were studied in Spain, like maritime pine pruning (forestry), grapevine and olive tree pruning (agriculture), and sawdust and marc of grape (industry residues), for its use in the circulating flow gasifier, to evaluate different typologies of biomass, independent of the provenance in the same equipment and conditions, with the objective of determining which materials can be used in gasification systems, whether combined or not. The results show that agricultural pruning wastes (olive and grapevine) presented higher gasification efficiency and yield than forestry (*Pinus pinaster* pruning) and industrial (marc of grape and sawdust) wastes, therefore, in the case of gasification, the agricultural wastes are more capable to produce a gas with high potential to be used for heat production or in the alternative, as power using the gas as working fluid through internal engines or gas turbines [163].

In Montpellier, two-stage gasifiers with a fixed bed were installed (the equipment can be used in pyrolysis and gasification) with the *Pinus pinaster* species as raw material. The pyrolysis was studied concerning different operational parameters. In relation to the biomass flow rate, when increased, a low quality of char was obtained. The best efficiency of the process (involving cracking, the heating value, and quality of the solid phase or charcoal and the gaseous phase) was obtained between 650 °C and 750 °C of temperature, 30 min residence time, and 10 and 15 kg h^{-1} of biomass flow rate, as the best conditions to optimize the pyrolysis process and obtain some products with high added value as charcoal production with an HHV of 33 MJ kg^{-1} and gases with an HHV of 15 MJ Nm^{-3} [121].

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